Formation of Bi,Pb-2223 and microstructural evolution in Pb-Ca-Cu deposited Bi-2212(001) single crystal by heat treatment

AUTHOR(S):

Kajihara, T.; Shimada, Y.; Hata, S.; Ikeda, K.; Nakashima, H.; Matsumoto, A.; Mochiku, T.; Kitaguchi, H.; Doi, T.

CITATION:

Kajihara, T. ...[et al]. Formation of Bi,Pb-2223 and microstructural evolution in Pb-Ca-Cu deposited Bi-2212(001) single crystal by heat treatment. Physics Procedia 2013, 45: 69-72

ISSUE DATE:

2013

URL:

http://hdl.handle.net/2433/235666

ELSEVIER
Available online at www.sciencedirect.com
SciVerse ScienceDirect
Physics Procedia 45 (2013) 69 – 72
Physics Procedia

ISS2012

Formation of Bi,Pb-2223 and microstructural evolution in Pb-Ca-Cu deposited Bi-2212(001) single crystal by heat treatment

T. Kajihara[a]*, Y. Shimada[a], S. Hata[a], K. Ikeda[a], H. Nakashima[a], A. Matsumoto[b], T. Mochiku[b], H. Kitaguchi[b], T. Doi[c]

[a]*Kyshu University, 6-1 Kasugakoen, Kasuga-shi, Fukuoka 816-8580, Japan*
[b]*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[c]*Kyoto University, Yoshidahonmachi, Sakyo-ku, Kyoto-shi, Kyoto 606-8317, Japan*

Abstract

In order to study the mechanism of phase transformation from Bi-2212 to Bi-2223, we fabricated Pb-Ca-Cu deposited Bi-2212 (001) single crystals as precursors of the Bi,Pb-2223 phase. These single crystals were heated in a sintered Bi-Pb-Sr-Ca-Cu-O pellet, and microstructure was observed by analytical electron microscopy. As a result of the microstructural observation around the Bi,Pb-2223 phase, two formation paths of Bi,Pb-2223 were recognized. One is the formation from a liquid phase which is formed by Bi-2212 and melting of the secondary phases such as $(Ca,Sr)_2PbO_4$ and CuO. The other is the growth of Bi,Pb-2223 into Bi-2212 phase by diffusion of Pb, Ca and Cu atoms along the <*hk*0> directions of Bi-2212.

Keywords: Bi,Pb-2223; Bi-2212 single crystal; Pb-Ca-Cu film; Phase transformation; Heat treatment; Scanning electron microscopy; Scanning transmission electron maicroscopy

1. Introduction

$(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi,Pb-2223) superconducting wire is expected for a wide range of applications such as power cables, magnets and so on. Toward actual use of the Bi,Pb-2223 wire, an increase of the critical current density (J_c) is desired. A possible solution is controlling microstructure. For example, it is effective to control crystallographic orientations of Bi,Pb-2223 crystal by reduction of voids and impurities. It is able to reduce the amount of low-T_c phases such as $Bi_2Sr_2CuO_{6+\delta}$ (Bi-2201) and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) in a Bi,Pb-2223 cable. In order to control the microstructure of a cable, the formation mechanism of Bi,Pb-2223 has been studied for several decades. The Bi-2223 single phase is hard to form from the synthesis of Bi, Sr, Ca and Cu sources. However, it is known that Bi,Pb-2223 single phase can be easily formed by doping Pb to Bi sites[1]. For the reason, Pb is used for raw materials in the fabrication of Bi-2223 wires by a powder-in-tube (PIT) method. In the PIT method, the rolling and heat treatment are repeated on wires filled with Bi,Pb-2212 powder fabricated by calcining Bi-Pb-Sr-Ca-Cu raw powder. During these heat treatments, Bi,Pb-2212 transforms to Bi,Pb-2223. The details of the phase transformation have not been clear yet, though there are several models of the phase transformation, such as Bi,Pb-2223 nucleation and growth from a liquid phase[2], intercalation of Ca and Cu atoms into Bi-2212 phase[3] and epitaxial growth of Bi,Pb-2223[4]. In this paper, we tried to obtain Bi,Pb-2223 phase by heat-treating a Pb-Ca-Cu deposited Bi-2212 (001) single crystals encapsulated in a Bi-Pb-Sr-Ca-Cu-O pellet, and examined the phase transformation process by electron microscopy observation.

*Corresponding author. Tel.:+81-92-583-7524; fax: +81-92-583-7546.
E-mail address: nk-t-kajihara@mms.kyushu-u.ac.jp.

doi:10.1016/j.phpro.2013.04.054

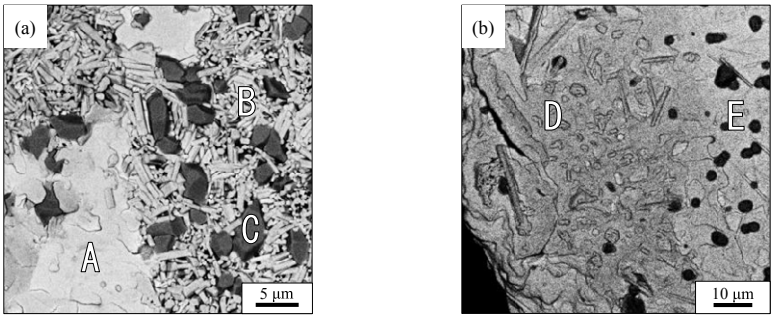

Fig. 1 (a) Plan-view SEM back-scattered electron image of sample 2 (EHT = 10 kV, WD = 3 mm). Constituent elements are Bi, Pb, Sr, Cu and O in a high-brightness and flat region A, Pb, Ca and O in a columnar structure region B, Cu and O in a low-brightness and granular-grain structure region C. (b) Plan-view SEM back-scattered electron image of sample 3 (EHT = 15 kV, WD = 3 mm). Constituent elements are Bi, Pb, Sr, Ca, Cu and O in both regions D and E. Region D has Bi-lean and Ca- and Cu-rich composition than region E.

2. Experimental

Bi-2212 single crystals of which the surface is (001) of Bi-2212 were fabricated by a travelling solvent floating zone method[5]. These single crystals were rectangular plates of 100-200 μm × 300-400 μm × 15-30 μm. The Pb-Ca-Cu film whose molar ratio was Pb : Ca : Cu = 1 : 1 : 1 was deposited on their horizontal (001) and vertical (*hk*0) surfaces at 300 °C for 2.5 h by a radio frequency sputtering method. The single crystal deposited by Pb-Ca-Cu is referred as sample 1. The Pb-Ca-Cu deposited Bi-2212 single crystals were heat-treated at 830 °C for 1 h or 30 h encapsulated in $Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{2.0}Cu_{3.0}O_x$ pellets. These heat-treated samples are referred as sample 2 and sample 3, respectively. The microstructure of these samples was observed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM), respectively. The SEM observation was carried out using Carl Zeiss ULTRA 55 operated at an accelerating voltage of 10 kV or 15 kV and the working distance of 3.0 mm and equipped with a backscattered electron detector. Under the observation condition, the SEM image intensity strongly depends on density differences in the sample. For example, Bi-2212 (density: 6.5 g/cm^3) region shows a lower image intensity than Bi-2201 (density: 7.03 g/cm^3) region. Specimens for TEM/STEM observation were prepared using a HITACHI FB-2000K focused ion beam (FIB) mill equipped with a microsampling system operated at an accelerating voltage of 30 kV. The TEM/STEM observation was performed with a JEOL ARM-200F electron microscope operated at 200 kV. STEM observation was conducted in a high-angle annular dark-field (HAADF) mode at a detection angle of 90-170 mrad. The incident beam-convergence angle for STEM was 16-18 mrad. The HAADF-STEM image shows a monotonic function relationship between image intensity and atomic number or density. Spatial distribution of constituent elements was analysed using a combination of SEM/STEM and energy-dispersive X-ray spectroscopy (EDX).

3. Results and discussion

3.1. Electron microscopy observation

The as-deposited Pb-Ca-Cu layer on the flat (001) surface of sample 1 was an amorphous layer where thickness was about 800 nm. Figure 1 shows typical plan-view SEM back-scattered electron images of sample 2 (a) and sample 3 (b). In Fig. 1(a), there are three characteristic regions: a high-brightness and flat region A, a columnar-grain region B and a low-brightness and granular-grain region C. From EDX analysis, constituent elements were Bi, Pb, Sr, Cu and O in region A, Pb, Ca and O in region B and Cu and O in region C. Although sample 3 showed similar plan-view microstructure to that of sample 2 in Fig. 1(a), the edge part of sample 3 exhibited different microstructure, as shown in Fig. 1(b). Region D is darker than region E in Fig. 1(b). From EDX analysis of regions D and E, both the regions contain Bi, Pb, Sr, Ca, Cu and O and region D has Bi-lean and Ca- and Cu-rich composition than region E.

Figure 2 shows cross-sectional HAADF-STEM images of region A (a) and regions B and C (h), and EDX elemental maps (b)-(g) acquired from the same view in Fig. 2(a). Figure 2(b)-(g) indicates that there are Bi-, Sr- and Cu-rich region and Pb- and Ca-rich region on the Bi-2212 single crystal of region A. In Fig. 2(h), there are some phases on the Bi-2212 single crystal. From EDX and selected-area diffraction (SAD) analyses, these phases in Fig. 2(h) were identified as $(Bi,Pb)_2Sr_2CuO_{6+\delta}$ (Bi,Pb-2201), $(Ca,Sr)_2PbO_4$ and CuO. Moreover, Bi,Pb-2201 phase exists in the Bi-2212 single crystal where shows is non-flat interfaces indicated by the white arrow in Fig. 2(h).

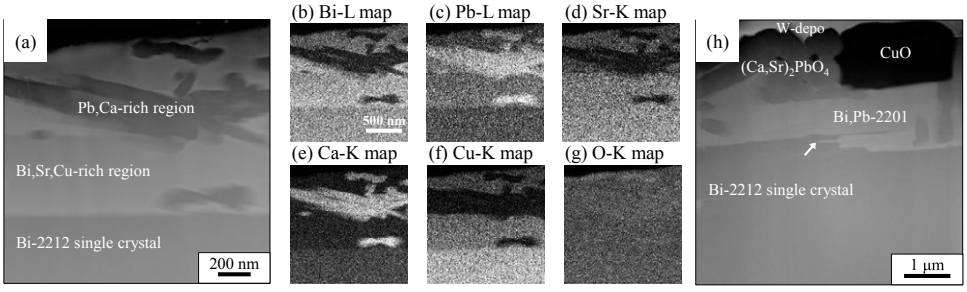

Fig. 2 (a) Cross-sectional HAADF-STEM image of region A in Fig. 1(a). STEM-EDX elemental maps for (b) Bi, (c) Pb, (d) Sr, (e) Ca, (f) Cu and (g) O acquired from the same field of view in (a). (h) Cross-sectional HAADF-STEM image of region B and region C in Fig. 1(a). The white arrow indicates the region where Bi,Pb-2201 phase exists in Bi-2212 single crystal. W-depo in (h) is protective layer for the sample during FIB processing.

Figure 3 shows the cross-sectional HAADF-STEM images of region D (a)-(d), and the EDX elemental maps (e)-(j) acquired from the white open square region in Fig. 3(d). The location of the original (001) surface of Bi-2212 single crystal is unclear in Fig. 3(a). EDX analysis revealed that thick Bi,Pb-2212 single crystal region F with 1 μm thickness is formed near the top surface region of sample 3. In Fig. 3(a), the two types of brightness regions formed on the Bi-2212 and Bi,Pb-2212 single crystals. Additionally, the region G where bright-line regions and dark-line regions which were orthogonal with [001] c-axis direction of Bi-2212 single crystal indicated by the black arrow formed in Bi,Pb-2212 single crystal region. In Fig. 3(b) which is a magnified view of the black open square region, there were bright-line regions: Bi-O layer and dark-line regions: Sr-O, Ca-Cu-O layer. From SAD patterns and high-resolution STEM images, the brightness region H on the left side of (b) was identified Bi,Pb-2212 and the darkness region I on the right side of (b) was identified Bi,Pb-2223. At the interface between region H: Bi,Pb-2212 and region I: Bi,Pb-2223, each (00*l*) plane contacts with 7-8° misorientation angle. Moreover, there is a same orientation relationship between region I and region J in Fig. 3(a) as well as Fig. 3(b). Figure 3(c), a magnified view of the white open square region indicated in (a), shows that there are Bi,Pb-2223, a half unit cell of $(Bi,Pb)_2Sr_2Ca_3Cu_4O_{12+\delta}$ (Bi,Pb-2234) and a half unit cell of $(Bi,Pb)_2Sr_2Ca_4Cu_5O_{14+\delta}$ (Bi,Pb-2245) along the <*hk*0> direction of Bi,Pb-2212 phase. In Fig. 3(d), there are Ca,Pb-rich phase and CuO near the side wall of Bi-2212 single crystal. Furthermore, EDX analysis revealed that Bi,Pb-2212 single crystal of over 5 μm thickness forms near the top surface region in the edge part of sample 3.

3.2. Microstructural formation behaviour during heat treatment

The results shown in *3.1* indicate the formation of some phases on the (001) surface of the Bi-2212 single crystal by the heat treatment for the Pb-Ca-Cu deposited Bi-2212 single crystal. For instance, Bi,Pb-2201, $(Ca,Sr)_2PbO_4$ and CuO by the heat treatment for 1 h, Bi,Pb-2212, Bi,Pb-2223, $(Ca,Sr)_2PbO_4$ and CuO by the heat treatment for 30 h. In Fig. 2(a), Bi, Sr, Cu and O compositions region and Pb, Ca and O compositions region formed on the Bi-2212 single crystal. This result indicates Bi and Sr supplied from a BSCCO pellet might be incorporated into the as-deposited Pb-Ca-Cu layer by the heat treatment in a BSCCO pellet. Bi,Pb-2201, $(Ca,Sr)_2PbO_4$ and CuO seen in Fig. 2(a) might be formed from Pb-Ca-Cu layer with Bi and Sr by the heat treatment for 1 h. Additionally, it is known Bi,Pb-2201 is the most stable phase of BSCCO phases in broad compositions and temperature range, and it is formed rapidly from a liquid phase[6]. The reason why Bi,Pb-2201 existed in the Bi,Pb-2212 at the white arrow region in Fig. 2(h), might be that Bi,Pb-2201 formed from a liquid phase by melting of the surface of the Bi-2212 single crystal by heat of reaction for creations of the secondary phases such as $(Ca,Sr)_2PbO_4$ and CuO.

There were less $(Ca,Sr)_2PbO_4$ and CuO phases on the surface of the region D in Fig. 1(b). Bi,Pb-2212 and Bi,Pb-2223 formed on the indistinct surface of Bi,Pb-2212 single crystals and the part of such regions had different c-axis directions from that of the Bi-2212 single crystal. These results suggest that Bi,Pb-2223 and Bi,Pb-2212 formed from liquid phases which were formed by melting of the Bi-2212 single crystal and the secondary phases which had been formed from the Pb-Ca-Cu layer with Bi and Sr atoms. On the other hand, Fig. 3(c) shows the Bi,Pb-2223 and half unit cells of Bi,Pb-2234 and Bi,Pb-2245 exists along <*hk*0> directions of the Bi-2212 phase. Moreover, Fig. 3(a) and Fig. 3(d) show that the closer to the side wall: (*hk*0) planes of the Bi-2212 single crystal, the larger Bi,Pb-2212 single crystal regions were formed. These results mean that Pb, Ca and Cu can enter the Bi-2212 phase from its (*hk*0) planes, and the including atoms can diffuse along <*hk*0> directions of the Bi-2212 phase easily. Therefore, it suggests that Bi-2212 near the exposure region of (*hk*0) planes such as step regions and side wall of the Bi-2212 single crystal, might form Bi,Pb-2223 by diffusion of Pb, Ca and Cu atoms along the <*hk*0> directions of the Bi-2212 phase.

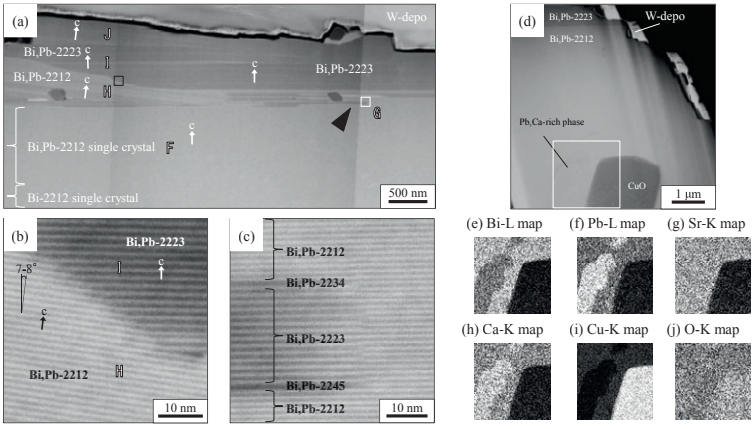

Fig. 3 (a) Cross-sectional HAADF-STEM image of the region D in Fig. 1(b). The white arrows indicate the [001] c-axis direction of each region. The black arrowhead indicates different contrast region G in the Bi,Pb-2212 single crystal. W-depo is protective layer for the sample during FIB processing. (b) A magnified view of the black open square region indicated in (a). The white arrow indicates the [001] c-axis direction of Bi,Pb-2223 and the black arrow indicates the [001] c-axis region of Bi,Pb-2212 in (b). (c) A magnified view of the white open square region indicated in (a). (d) Cross-sectional HAADF-STEM image of the side wall of the region D in Fig. 1(b). STEM-EDX elemental maps for (e) Bi, (f) Pb, (g) Sr, (h) Ca, (i) Cu and (j) O acquired from the white open square region in (d). W-depo is protective layer for the sample during FIB processing.

4. Conclusion

By the observation of microstructures in Pb-Ca-Cu deposited Bi-2212 (001) single crystals by the heat treatment in a BSCCO pellet, the following conclusions have been obtained.

(1) Bi,Pb-2223 forms by the heat treatment of the Pb-Ca-Cu deposited Bi-2212(001) single crystal.
(2) In the initial heat treatment, Bi and Sr atoms supplied from a BSCCO pellet enter the deposited Pb-Ca-Cu layer. Bi,Pb-2201, $(Ca,Sr)_2PbO_4$ and CuO are formed from this layer and a liquid phase which is formed by melting of the surface of the Bi-2212 single crystal .
(3) As heat treatment progress, Bi,Pb-2212 and Bi,Pb-2223 form on the Bi-2212 single crystal from a liquid phase which is formed by melting of Bi-2212 and the secondary phases such as $(Ca,Sr)_2PbO_4$ and CuO .
(4) Pb,Ca and Cu atoms enter Bi-2212 from (*hk*0) planes of Bi-2212 preferentially. Bi,Pb-2223, Bi,Pb-2234 and Bi,Pb-2245 form by diffusion of Pb, Ca and Cu atoms along the <*hk*0> directions of the Bi-2212 phase.

Acknowledgements

This work was partially supported by KAKENHI (22246079) with a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

[1] M. Takano, J. Takeda, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda *et al*., Jpn. J. Appl. Phys. 27 (1988) L1041-L1043.
[2] J.-C. Grivel, R. Flükiger, J. Alloys Comput. 235 (1996) 53-58.
[3] Y.-L. Wang, W. Bian, Y. Zhu, Z. -X. Cai, D. O. Welch, R. L. Sabatini *et al*., Appl. Phys. Lett. 69 (1996) 580-582.
[4] P. E. Morgan, R. M. Housley, J. R. Porter, J. J. Ratto, Physica C 176 (1991) 279-284.
[5] T. Mochiku, K. Hirata, K. Kadowaki, Physica C 282-287 (1997) 475-476.
[6] T. Suzuki, K. Yumoto, M. Mamiya, M. Hasegawa, H. Takei, Physica C 301 (1998) 173-184.